



An over review on recently developed techniques, mechanisms and intermediate involved in the advanced azo dye degradation for industrial applications

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ABSTRACT

The continuous growth of population and increasing industrial activities in the different sectors, viz., textiles, leather, plastics, cosmetics and food processing industries require the development of varying nature of novel dyes. Among the dyes used in different industries, azo dyes are considered to be the most widely consumed and play an important role in the dyeing of textiles, leather, and plastics, etc. Azo dyes and their degradation products are toxic toward aquatic life and mutagenic for humans. The textile industry is one of the major contributors of azo dye pollutants and discharges the large quantity of azo dye effluents, which causes an acute hazardous effect on environment and human health. The conventional physical and chemical methods adopted to degrade azo dye effluents are not always efficient, due to the factors such as pH, temperature, and concentration of dyes. The existence of drawbacks on physico-chemical methods on the degradation of azo-dyes has triggered an interest for the researchers around the world to develop cost effective, alternative and eco-friendly techniques. Even though, the recent available reports indicate that the nanoparticles based microbial enzyme conjugates is considered to be an efficient technique to remove the azo dye from textile effluents within a few minutes, however, they are very high cost and possess difficulties in scale-up. In the present work, an attempt has been made to bring the relevant detailed literature available with regard to effective and efficient method and mechanism of degradation of azo-dyes in order to benefit the researchers of both from academia and industry. Furthermore, the present article also provides degradation based on their chemical structure and the conditions, in addition to mechanism involved for the bio-degradation and photo-catalytic degradation of azo dyes including merits and demerits of the each method.

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1. Introduction

In an early 19th century, the dyes were initially obtained from natural sources for coloring the fabric materials. Dyes were also used before the nineteenth century, which were obtained from either of vegetable (*i.e.*, weld, madder, indigo) or animal origin (*i.e.*, cochineal, shellfish) and they belong to chemical types such as flavonoids (yellow), anthraquinones (red) and indigoids (blue and violet) [1]. Mauveine was the first synthetic dye synthesized in the year 1856 and up to 1970, nearly about 60% of the man-made dyes used were synthetic in nature [2]. There are numerous types

of synthetic dyes available in the market at present and are produced annually about hundreds of thousand tons worldwide [3]. It is well known that the dyes are synthetic aromatic organic compounds, which are normally used for coloring/dyeing different substrate materials for esthetic and other functional applications. The textile industry is one of the major consumer of different synthetic dyes and plays major role in the economical growth of the country. During textile processing, inefficiencies in dyeing result significant loss of dyestuffs (ranging between 20% and 50% based on the nature of dyes), and is being directly drained out to water bodies as wastewater, which ultimately pollute the environment. Among the different category of dyes, azo dyes are considered to be recalcitrant, non-biodegradable and persistent [4–5]. Hence, the treatment of dye based water effluent is considered to be one of the most challenging task with respect to the concern of the environ-

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mental fraternity [6]. Some of them are potential and dangerous to living organisms due to their possible toxicity and carcinogenicity. Disposal of azo dyes from textile processing industries and other dyeing related industries into the water resources causes numerous environmental problems like reduction in water transparency and dissolved oxygen [7], which shows a negative impact on germination and growth of plant species that imbalances the ecological function. Dyes may also significantly affect the photosynthetic activity in aquatic life by preventing light penetration and consequently toxic to aquatic fauna and flora due to the presence of aromatic compounds, metal salts, chlorides, etc. Therefore, the removal of dyes from textile effluent is warranted [8,9].

1.2. Classification of dyes

The compounds which absorb electromagnetic energy in the visible range (~350–700 nm) are colored and these colored compounds are mostly known as dyes. Dye molecules possess both chromophores (delocalized electron systems with conjugated double bonds) and auxochromes (electron-withdrawing or electron donating groups, which intensifies color). An example for chromophores are $-C=C-$, $-C=N$, $-C=O$, $-N=N$, $-NO_2$, quinoid rings, etc., which imparts color to the dye molecules and an example for auxochromes are $-NH_2$, $-COOH$, $-SO_3H$, $-OH$, etc., which intensifies the color of the chromophore by altering the overall energy of the electron cloud of the molecular system [10]. The dyes are classified on the basis of chemical structure or chromophore viz., azo (mono-azo, di-azo, tri-azo, poly-azo), anthraquinone, phthalocyanine, diarylmethane, triarylmethane, indigo, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, amino ketone, hydroxyl ketone stilbene and sulfur dyes [11–18].

1.3. Obligation of degradation

Dyes are the colored substances that are applied on different substrates like textiles, leather and paper products, etc., primarily for esthetic appeal by using different dyeing methods. Apart from natural dyes, synthetic dyes are predominantly synthesized from petroleum based precursor derivatives and earth mineral based raw materials, they are also classified based on the mode application as well as chemical constituents namely azo dyes, direct dyes, disperse dyes, sulfur dyes, pigment dyes, vat dyes, mordant dyes, reactive dyes, aniline dyes, anthraquinone dyes, developed dyes, naphthol dyes, macromolecular dyes, metalized dyes, pre-metalized dyes and gel dyeing, etc. Among the different class and form of dyes, azo dyes are considered as the oldest class and largest form of industrially produced organic dyes due to their suitability and versatile application for different substrate materials [19,20]. There are about 3000 azo-dyes currently manufactured and used all over the world for wide range of industrial applications.

The most of the azo dyes used for dyeing of different substrates are primarily in the form mono-azo compounds, which have the common structural unit of the azo ($N=N$) chromophore that are normally linked by two aromatic molecular systems and the textile industry is considered to be the largest consumer of azo dyes [21]. Heterocyclic structured dye molecules have pronounced bathochromic shift [23] and they are not only used as coloring purpose, they are also widely utilized for different therapeutic applications such as antiseptics [24], antimicrobial [25], anti-diabetics [26], anti-neoplastics [27], transmissible spongi form encephalopathy [28], anti-ulcerative [29], antioxidant [30], analgesic [31], anti-inflammatory [32], anti-tubercular [32], antiviral [33], and antitumor [34] activities. In addition to dyeing and therapeutic purpose,

the azo- compounds are involved in a wide range of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis, and nitrogen fixation [35]. The azo dyes are also find application in dyeing of textile fibers, biomedical studies, and advanced organic synthesis [36]. The high-tech areas like lasers, liquid crystalline displays, electro-optical devices and ink jet printer [37], the azo-dyes are significantly used. Their biological activities make them useful [35] antibacterial [38] and pesticidal [39], anti-septic and antiprotozoal applications including wound healing.

Although some of the azo dyes have been reported to be non-toxic, but most of the azo-dyes used in the various industries are not eco-friendly and the resulted waste water affect the aquatic life and thus, ecosystem. The azo dyes are essential for day to day industrial activities and most importantly used for dyeing on cellulosic fiber, protein fiber, and synthetic fibers. During the industrial process (textile, leather and food, etc.), all the dye molecules used do not get fixed on the fibers or other substrate materials and significant portion of the dyes are unused and discarded as waste in the form of effluent, which pollutes the environment [22]. Hence, it is most warranted to use the dye-stuffs capable of degradable by microbes or alternative methodology is required to degrade or remove the dyes from the industrial waste water.

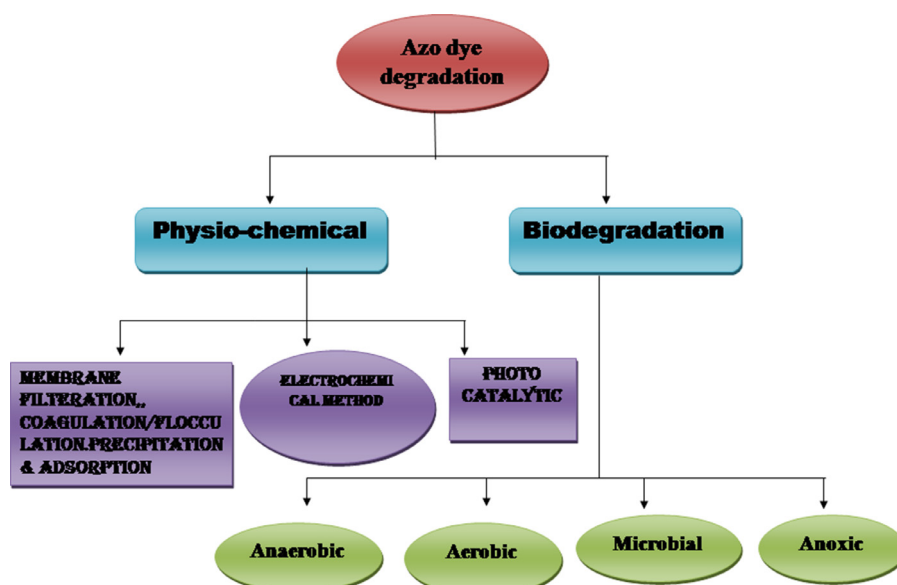
1.4. Environmental concern of dyes

Most of the dyes are visible their concentration as low as 1 mgL^{-1} . Textile-processing units releases highly colored water effluents with a dye content in the range of $10\text{--}200 \text{ mgL}^{-1}$ [40], which causes both environmental as well as esthetic problem to the water bodies. As dyes are designed to become stable towards chemical and photological process, hence, they are highly persistent in natural environments. The dyes present in the waste water expected to cause serious eco-toxic problems and consequently contributes to the potential danger of bio-accumulation and human food chain.

1.5. Toxic effect of azo dyes

Dye has been an integral part of the socioeconomic component since 2000 BC (before christ) and the use of synthetic dye becomes predominant only after the industrial revolution in particular to textile processing industries [41]. Out of more than 900,000 tons of dyes produced annually, 70% of them are belongs to azo group based dyes [42]. Most of the dyes used in textile processing are known only by their trade name and not by their actual chemical nature and this led to serious problems to find suitable and complete dye degradation process. Textile industries release a huge amount of colored effluent to the nearby water bodies with inefficient effluent treatment causes the major environmental pollution. Owing to their xenobiotic and wayward nature, the azo dyes possess a long-term effect on life due to the presence of significant amount of toxic metals and chemicals with enhanced pH.

In addition to change of color of water bodies like lakes and rivers by the dyes contaminated effluents, they tend to undergo chemical and biological changes which consume dissolved oxygen and consequently led to kill the fishes, and destroy other aquatic organisms. Some dyes possess toxicity that is hazardous to aquatic life and causes serious health problems to human through the food chain process. Further, the textile dyeing effluents are also known to cause extreme variations of pH, dissolved oxygen (DO), temperature, chemical oxygen demand (COD) and dissolved salts of the receiving water bodies [43–45]. An aqueous solution of azo dyes possesses the pH normally in the range of $2\text{--}10$ [46–47]. Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed (i.e. demanded) by aerobic biological organisms to break down the



Scheme 1. Treatment methods used for the removal of azo dyes from industrial effluents.

organic material present in a given water sample at certain temperature over a specific time period and the BOD of azo dyes are in the ranges of 80–6000 mg/L [48,49]. Furthermore, chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the chemical decomposition of organic matter and the oxidation of inorganic chemicals [50–53] present in the water body, which was obtained from the effluent released from various industries and COD of azo dyes are in the range of 150–12,000 mg/L.

It also unbalances the organic-inorganic chemical content of the environment and it affects the biotic content present in water. When dye gets mixed with water, light penetration efficiency decreased inside the aquatic system and hence, the water ecosystem gets affected. Toxic materials present in the azo dyes, when contaminated with water bodies can enter into fishes or other aquatic animals, which are further taken up by human causing hypertension, sporadic disorder, cramps, etc. with prolonged effect. Further, it was observed that the benzidine based azo dyes have been recognized as a carcinogen in human urinary bladder and tumorigenic in laboratory animals [54]. It can also cause hepatocarcinoma, splenic sarcoma, nuclear anomalies in experimental animals, and also chromosomal aberrations in mammalian cells [55]. Due to easy inhalation or its ready solubilization in water, the azo dyes can cause fast absorption by the skin leading to risk of allergic reaction, cancer, eye irritation, etc. [54]. Para-phenylene diamine (PPD) is considered as one of the major component of azo dyes. PPD containing azo dyes are toxic and causes contact dermatitis, chemosis, lacrimation, exophthalmos, and permanent blindness. Ingestion of PPD products contribute to the rapid development of edema on face, neck, pharynx, tongue and larynx along with respiratory distress [56]. This is because of the reduction of azo dyes led to the formation of aromatic amines, which gets metabolically oxidized to reactive electrophilic species and consequently binds covalently to the DNA through an irreversible process. Some of the important azo dyes, applications and their adverse effects are presented in Table 1.

1.6. Classifications of azo dyes degradation

Azo dyes from textile effluent water have been degraded by physicochemical and biological techniques to remove color from

the dye containing wastewaters. In this regard, each technique has its own limitations and advantages, which includes the factors such as nature of dyes, composition and concentration of wastewater, hazardous nature of effluents, cost of required chemicals, handling and operational costs. These factors decide the technical and economical feasibility of each method of treatment of effluent water and degradation or removal of dyes. The by-products formed during the degradation process are also control the feasibility of the dye removal process and the use of one individual process may often not sufficient to achieve the complete degradation or removal process. Hence, the process of removal and degradation of dyes are emerging and vital area of research, which can motivate the research activities to mitigate the environmentally associated problems with textile dye effluents to protect the environment. The different treatment methods used for the removal of dye from various industrial waste waters are presented in Scheme 1.

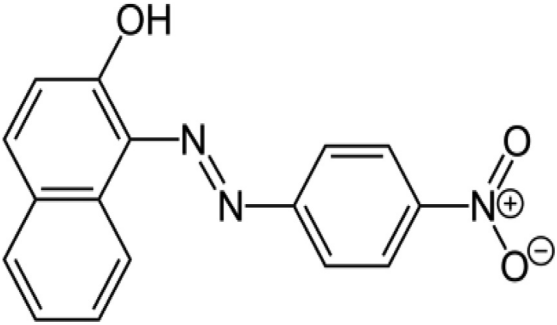
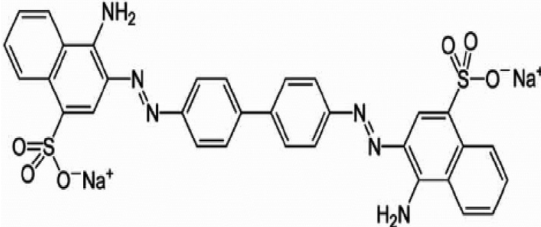
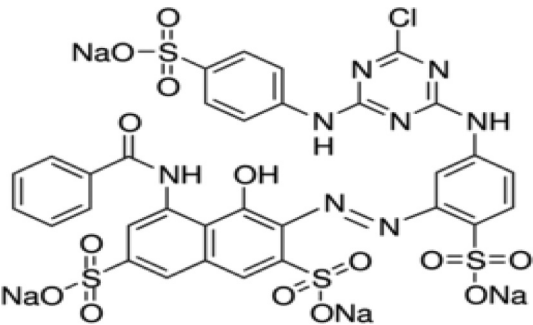
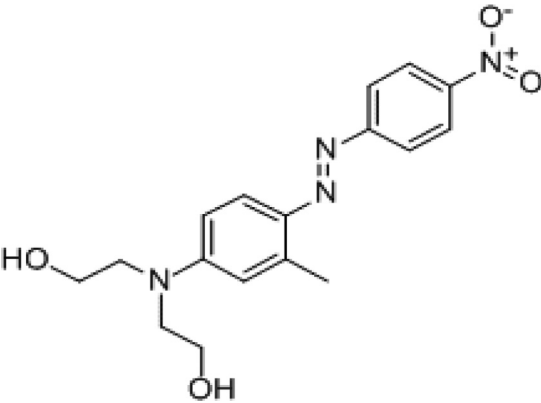
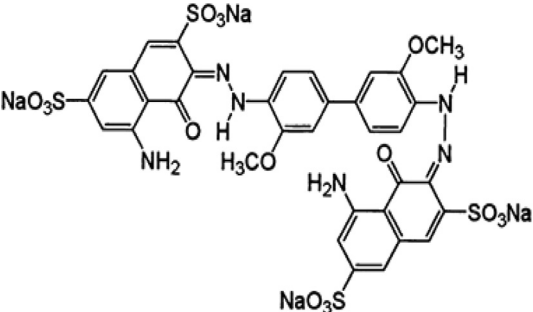
1.7. Biodegradation of azo dyes

Degradation (decoloration) of azo dyes can be possible by using different kinds of bacteria and the reductive cleavage of $-N=N-$ bond is the primary step of the degradation process. Different types of biodegradation and decoloration of azo dyes that are carried out under different experimental conditions are explained in the following section.

1.7.1. Degradation of azo dyes under anaerobic conditions

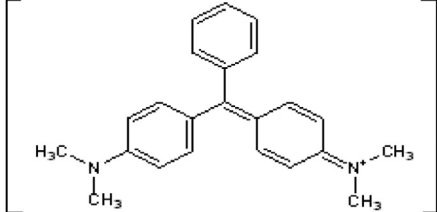
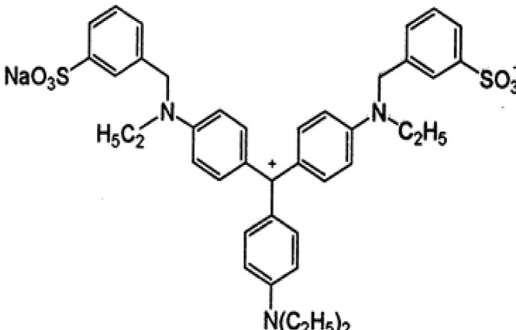
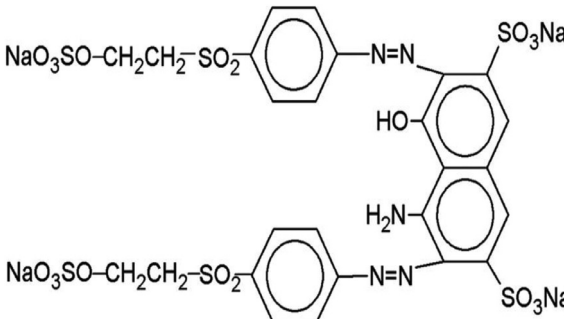
Anaerobic degradation of dyes present in the wastewater is a promising technology, which is relatively simple and nonspecific reduction process of azo-dyes. During the direct enzymatic catalysis, non-specific azo-reductase microorganisms directly catalyzes the reduction process of azo dye. However, the existence of this enzyme has not been directly verified till now and further the reduction process relying on cofactors and redox intermediates formed during the dye degradation process need to be ascertained. Thus, the mechanism may be depends on the redox intermediate products formed during the degradation of azo dyes under anaerobic conditions. At present, the reported and predicted redox active coenzyme intermediates are FAD (flavin adenine dinucleotide) and NAD(P)H (nicotinamide adenine dinucleotide phosphate oxidase) [65,66] and they can receive electrons from an azo reductase

Table 1
Azo dyes, applications and their hazardous effects.

Azo dye	Structure	Application	Hazardous effect
Red dye		Can be applied on synthetic and natural fibers, leather, paper, and phenol-formaldehyde resins.	Human urinary bladder cancer and malignant tumors in female rats and other laboratory testing animals [57]
Congo red		Used to dye the cotton fabric, pH indicator and biological stain.	Benzindinem byproduct causes mutagens and carcinogenic effect [56]
Reactive brilliant red		Used widely in textile industries, drugs, personal care products (cosmetics, tattoo inks, hair dye), food colorants, and inks for printing.	Muscle contraction or spasticity, Inhibit human serum albumin, bind to body protein or enzyme, and cause alteration of function [58]
Disperse Red		Used as dye in variety of industries like plastics and textiles industry to dye polyvinyl chloride, polyvinylacetate, polyester, polyamide, polyacryl and polyurethane materials including synthetic fibers, and foam materials (e.g. polyurethane foams).	Somnolence (general depressed activity). Mutagenic to human beings and salmonella, (First evaluated using micronucleus assay in human lymphocytes), which affect the activity and composition of microbial communities [59–60]
Direct Blue 15		Mostly used for cotton, such as glue the cellulose fiber, silk and rayon. It was also used for pulp, biological, film footage of dyeing, and used to make the ink. Used in biological and staining applications.	Mutagenic effect due to reduction process, and also having strong carcinogenic effect [61]

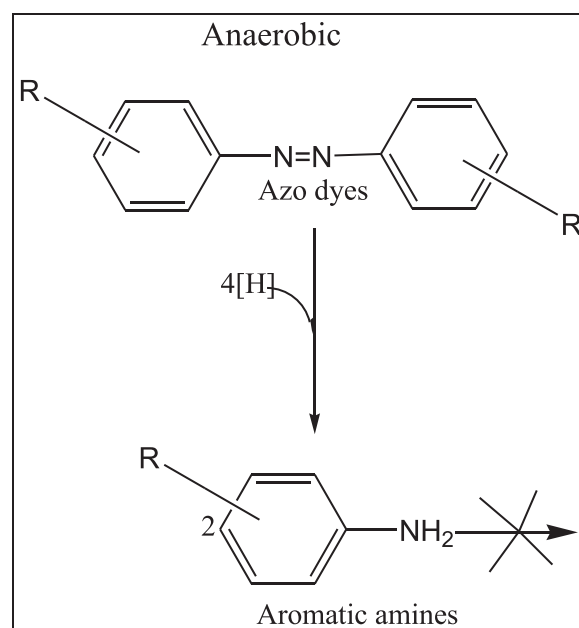
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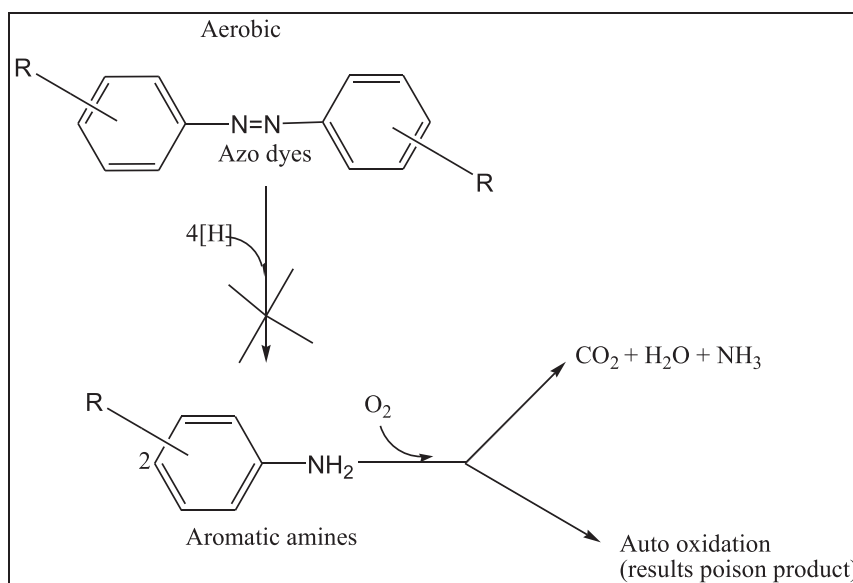
Azo dye	Structure	Application	Hazardous effect
Malachite Green		Used as dye in silk, leather, paper and controversially used as antimicrobial in aquaculture.	Carcinogenesis, mutagenesis, chromosomal fractures, and respiratory toxicity. Significant change in biochemical parameters of blood for malachite green-exposed fish and histopathological effects include multi-organ tissue injury [62]
Acid Violet 7		It was mostly used in textile industries along with food, paper, and cosmetic industries.	Chromosomal aberration, acetylcholinesterase activity inhibition, membrane lipid peroxidation [63].
Reactive Black 5		Used as dye stuff to dye cotton and other cellulosic fibers, wool and nylon.	Restrict nitrogen use efficiency of the plant, decrease the urease activity, mutagenicity, and causes carcinogenicity [64]

and then subsequently transfer the electrons to the azo dye. During the process, the azo-bonds ($-N=N-$) present in the dyes are cleaved to produce aromatic amines (reduction of azo-bonds), and thus removes the color of the effluent (Scheme 2).

According to the related reports [66] available, the redox potential of 50 mV is required for the effective decoloration of azo-dyes under an anaerobic conditions. This report also ascertains that the occurrence of spontaneous non-specific reduction reaction between the azo dye and the formation of intermediates depends on the red-ox potential of the catalysts. However, the cleavage of the chromophore groups of dyes results colorless, odorless, and toxic intermediate metabolites of aromatic amines, which are commonly mineralized under aerobic conditions. In addition, it was important to note that even though many of these cultures were grown by aerobically, the decoloration was achieved only under anaerobic conditions through enzymatic red-ox process. Furthermore, it has been reported that the presence of oxygen usually suppresses the reduction activity of the azo ($-N=N-$) linkage because of aerobic respiration may dominate the utilization of NADH and impede the transfer of electrons from NADH to the di-azo bond. In addition, it has also been reported that aromatic amines containing functional hydroxyl and carboxyl groups can be mineralized under anaerobic condition. Some of the aromatic amines, which are prone to undergo self-oxidation can be degraded under anaerobic conditions [66].



Scheme 2. Cleavage of Azo-dyes in the presence of azo reductase enzyme under anaerobic process (azo dye + enzyme complex).



Scheme 3. Cleavage of azo-dyes and aromatic amines during the aerobic treatment.

1.7.2. Degradation of azo dyes under aerobic conditions

Dye degradation under aerobic conditions is mainly catalyzed by enzyme called azo-reductase. Reports also indicate that some aerobic microorganisms were also used along with azo reductase enzyme to improve the kinetics of the dye degradation process. The factors such as concentration of dyes, concentration of enzymes, temperature, and rate of intermediate complex formation also contribute and influence to the reduction of azo-dyes. It is well known that mostly the degradation of azo-dyes produces the aromatic amines as intermediate metabolite products, which are subsequently degraded by microorganisms under aerobic conditions in order to achieve the complete mineralization of azo dyes according to [Scheme 3](#) [67]. Further, it was also observed that the aerobic treatment of azo-dye effluents is an ineffective in most of the textile water treatment process even though few microorganisms degrade the dye molecules partially or completely. However, the amine products formed during an anaerobic process can be further de-mineralized or decomposed by aerobic treatment process.

1.7.3. Conventional activated sludge treatment

Conventional activated sludge treatment process is one of the important methods of aerobic treatment process for azo-dye degradation process particularly to stabilize dye metabolites intermediate products. Further, the conventional activated sludge treatment of wastes is often an effective and highly economical method of reducing organic pollutants present in the effluent water. A fair amount of research has been conducted to assess the viability and feasibility of using activated sludge for the textile effluents treatment process [68–71]. However, an aerobic treatment of azo dye waste has proven to be an ineffective process in most of the cases, but anaerobic process is often currently used typical method for the treatment of azo-dye effluents discharged from different industrial sources [72,73]. This is because of the rate of degradation of azo-linkages is significantly lower in the presence of aerobic microbes compared to that of anaerobic process. In other words, the ability to destroy dye chromogens by the aerobic microbes are lesser than that of anaerobic bacterium. However, the aerobic sludges have been successfully used to stabilize dye metabolites intermediates [74].

1.7.4. Microbial decoloration and degradation of dyes

From the recent studies, it was inferred that the microbial degradation of wastewater was mainly focused on the breeding of a variety of decoloration strains with enhanced efficiency. The azo-dyes can be decolorized by a wide variety of microorganisms including bacteria, fungi, actinomycetes, algae and so on. The decoloration efficiency of azo-dyes is also depends on the growth environment and metabolism mechanism involved in the presence of different microorganisms. Therefore, it is very important to understand the mechanisms that involved during the decoloration process and to study the degradation of different microorganisms for creating a suitable living environment for micro-organisms, which contributes to the decoloration and degradation of azo-dyes [75].

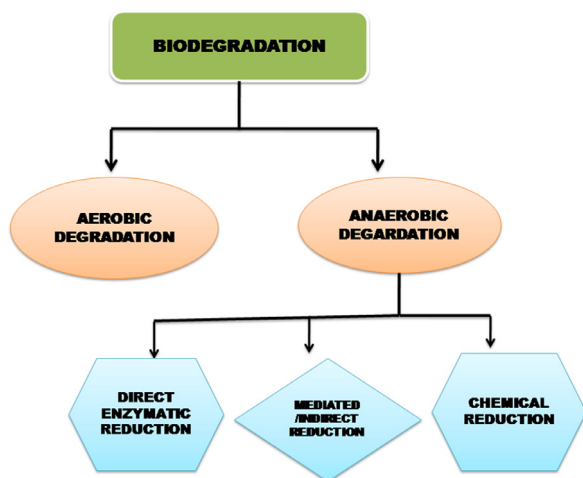
1.7.5. Degradation of azo dyes under anoxic conditions

Anoxic decoloration of azo-dyes are carried-out by mixed aerobic and facultative microbial consortia [76–80]. For example, pure bacterial strains such as *Pseudomonas* and *Proteus mirabilis* can decolorize the azo-dyes under anoxic conditions [81–83]. Azo-dye decoloration process requires the cultures that was generally made from complex organic sources such as yeast extract, peptone, or a combination of complex organic source and carbohydrate [84].

1.8. Mechanism of biodegradation

The processes involved in the biodegradation of azo-dyes are shown in [Scheme 4](#). The efficient method of color removal by bacterial cells was done through the adsorption of dye onto the biomass, which is similar to other physical adsorption mechanisms. Color removal using an adsorption principle method was not most suitable for long term treatment, because of dye molecules get concentrated onto the biomass during the adsorption and become saturated with the short time period, and the accumulated dye-adsorbents should also need to be disposed. Hence, the interaction between the dye molecule and bacterial cell is the first step in the biological reduction of azo- dyes, which is a destructive treatment technology.

After the physical adsorption, which is the initial step of the bio-degradation process of dyes, the process of bacterial azo-dye degradation consists of two stages. The first stage involves the reductive cleavage of the dye's azo-bond ($-N=N-$), resulting in the



Scheme 4. Various process or steps involved in the biodegradation of azo-dyes.

formation of aromatic amines, that is generally colorless but potentially hazardous in nature. The second stage involves degradation of the aromatic amines under aerobic conditions.

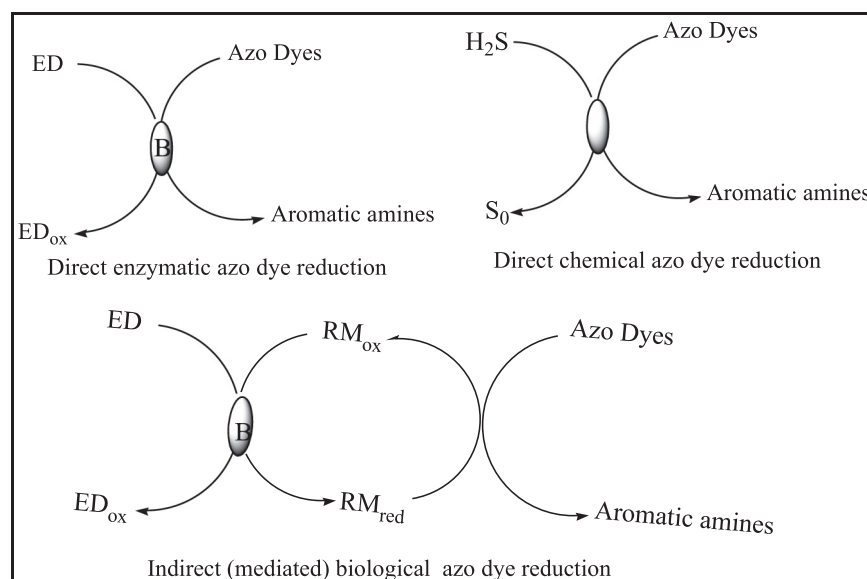
Further, azo-dye reduction with the help of azo-reductase under anaerobic conditions involves transfer of four-electrons (reducing equivalents), which proceed through two stages at the azo-linkage and in each stage two electrons are transferred to the azo-dye, which acts as a final electron acceptor resulting in decoloration of dyes. The resulting intermediate metabolites are further degraded aerobically or anaerobically [64,85]. Hence, in general, azo dyes can be biologically degraded by any one of the following mechanism (Schemes 4 and 5) listed below as per above discussion [86]. However, the presence of oxygen usually inhibits the reduction activity azo-bond since, an aerobic respiration may dominate the utilization of NADH and thus hindering the electron transfer from NADH to azo bonds. Hence, the azo dye degradation may take place more favorably through any one of the three anaerobic dye degradation (Scheme 5) mechanisms [87,88].

1.8.1. Direct enzymatic reduction

The bacterial decoloration of dyes is being facilitated by various reductive enzymes such as azo-reductase, nicotinamide adenine dinucleotide hydrogen (NADH)-dichlorophenolindophenol (DCIP) reductase (NADH-DCIP reductase), malachite green reductase (MG reductase) and oxidative enzymes like lignin peroxidase and laccase. Further, this direct enzymatic reduction method of dye degradation can be explained by using mixed system of NADH-DCIP reductase and MG reductase. Here, NADH-DCIP reductase belongs to the bacterial mixed function oxidase system and take part in the detoxification of xenobiotic compounds [89]. The NADH-DCIP reductase reduces the DCIP using NADH as an electron donor. DCIP is blue in color in its oxidized form and becomes colorless after reduction. The significant induction of nonspecific reductase in the biodegradation of malachite green, which is termed as MG reductase and this MG reductase reduces the malachite green into leucomalachite green using NADH as an electron donor [90].

1.8.2. Indirect/Mediated biological reduction

High molecular weight sulfonated azo dyes are unable to pass through the cell membrane and therefore, the reduction of these dyes occur through the mechanism that is not dependent on the transport into the cell membrane. From the earlier reports [91–93], it was believed that the role of redox mediators is to reduce or break the azo-bond in the dye molecules present in waste water using bacteria under anaerobic conditions. It is also observed that the addition of riboflavin in small amounts significantly enhanced the reduction of Mordant Yellow 10 using anaerobic granular sludge. Further, the addition of 1-amino-2-naphthol to Acid Orange 7, which is one of the constituents of Acid Orange 7 (azo-dye) increases its decoloration rate by mediating the transfer of reducing equivalents [94]. In addition, the addition of synthetic electron carriers such as anthraquinone-2–6-disulphonate to many azo-dyes could also greatly enhance their decoloration rates [92]. Further, it was also reported that [91] the redox mediators formed during anaerobic cleavage of azo dyes can promote the rate of aerobic degradation of xenobiotic compound. Cell suspensions of *Sphingomonas* sp. strain BN6 grown aerobically in the presence of 2-naphthyl sulfonate (NS) also exhibited 10–20 fold increase in the decoloration rate of an azo dye amaranth (short-lived perennial plants) under anaerobic conditions. Even the addition of culture fil-



Scheme 5. Schematic representation of the various mechanisms proposed to involve for the reduction of azo dyes present in the wastewater {Where, RM = Redox mediator; ED = electron donor; b = bacteria (enzymes)}.

trates of these cells are enhancing the anaerobic decoloration by cell suspensions grown in the absence of NS. Hence, the redox intermediates generated during aerobic degradation of aromatic compounds could also enhance the dye decoloration [91]. For example, the addition of culture supernatant containing metabolites of a dye-decolorizing *E. coli* NO₃ strain enhanced the azo-dye decoloration rate [85]. From the above studies, it was concluded that the indirect or mediated biological reduction process is a phenomenon in which the rate of dye degradation could be increased by the addition of any compound or the intermediate compound formed during the dye degradation or cell culture process as the mediators for biological reduction process.

1.8.3. Chemical reduction

Dye decoloration can also occur by chemical reactions with inorganic compounds (sulfide and ferrous ion) that are formed or regenerated as end products of metabolic reactions under anaerobic conditions. The decoloration of azo dyes was done by H₂S generated from sulfate reducing bacteria resulted in the extracellular process. sulfate ions produced from biogenic sulfide under methanogenic conditions can also influences the dye reduction process. Various inducers and stabilizers of oxido-reductive enzymes are CaCO₃, indole, o-touludine, veratrole and vanillin, which also enhances the dye decoloration process [95]. Further, the analysis of decoloration kinetics in the batch reactors and the laboratory scale anaerobic sludge bed reactors indicate the relative importance of chemical dye reduction mechanism for the high rate of reduction of dyes from anaerobic bio-reactors.

1.9. Physio-chemical degradation

Apart from enzymatic or microbial degradations process, several other techniques have been used for the removal of dyes from industrial effluents. For practical and commercialization process, wastewaters are usually treated by physical or chemical processes [91,96–102]. Physico-chemical techniques include membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, and advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photocatalytic oxidation).

1.9.1. Membrane filtration

Nano-filtration and reverse osmosis using membranes with a molecular weight cut-off (MWCO) below ~10,000 Dalton, can be applied as main or post treatment processes for the separation of salts and larger molecules including dyes from dye-bath effluents and bulk textile-processing wastewater. Filtration with high porous membranes, i.e. ultra-filtration and microfiltration are generally not suitable as the membrane pore size is too large to prevent dye molecules passing through, but it can be successful as pre-treatment for further nano-filtration or reverse osmosis process.

The nano-membrane filtration is a quick method with low spatial requirement and has advantage like some of the concentrated compounds including non-reactive dyes can be separated and reused [103,104]. The reuse process can be feasible only for flow of effluents with lower rate [105]. The important disadvantages of membrane techniques are flux decline and membrane fouling, which is necessitating the frequent cleaning and regular replacement of the modules or component of the waste water treatment plants. Another important drawback is that the generated concentrate or waste materials must be processed for further oxidation process [106]. Even though the capital costs of the membrane used in this filtration technique are high and such a filtration techniques for the treatment of textile wastewaters are widely applied in South Africa [107].

1.9.2. Coagulation/flocculation

Coagulation/flocculation is often applied in the treatment of textile-processing wastewater to remove *Chemical Oxygen Demand* (COD) and color from the raw wastewater before further treatment [108–110] to polish the final effluents by biologically or otherwise treated wastewater [111,112] or even as the main treatment process [113]. The principle of the process is the addition of the coagulant such as lime, magnesium, iron and aluminum salts to the polluted water may led to rapid chemical association between the coagulant and the pollutants and thus, flocs or precipitate will be formed can be removed from the water phase through filtration process. However, these inorganic compounds are generally not very suitable to remove highly soluble (=sulphonated) dyes from solution [114,115] unless rather large quantities are dosed. In addition, the coagulation/flocculation with inorganic chemicals generates considerable volumes of useless or even toxic sludge that must be incinerated or create problems related to disposal, which requires high cost and environmental related issues. However, recently developed organic polymers have been proven highly effective as dye coagulants and the sludge production associated with polymer dosing is relatively lower when compared to that of inorganic coagulants [101,116]. Most of the polymers used for color removal are cationic and they are toxic to aquatic life even at very low concentrations (less than 1 mg/L). The cationic polymers as coagulant treated wastewater have been found to inhibit the nitrification process of the microorganism in the plants [117].

1.9.3. Electrochemical degradation

Over the past 10 years, the electrochemical techniques have found a special interest for wastewater remediation [118]. The electrochemical techniques used for dye removal can be classified as electro-coagulation, electrochemical reduction, electrochemical oxidation, indirect electro-oxidation with strong oxidants (electro-oxidation with active chlorine, electro-Fenton), and photo-assisted electrochemical methods (photo electro-Fenton, photo electro-catalysis) [119]. These electrochemical techniques are more compatible with the environment and this is because the electrons alone are involved for these electrochemical processes [120]. They also have advantages such as the use of simple equipment, easy operation, lower operating temperature, etc. [121]. It is interesting to note that the higher quantities of removal of polluting substances can be done with effective energy resource management i.e. minimum energy with maximum amount of dye can be removed. The electric current induces redox reactions upon the electrodes surface resulting in the transformation and destruction of the organic compounds, which results complete oxidation to CO₂ and H₂O in accordance with the following generalized mechanism.

Electrochemical oxidation (EO) of dyes can be done in electrochemical cell by any one of the following methodologies.

- 1) **Direct anodic oxidation** in which the redox reaction takes place during the cyclic process (At anode oxidation and cathode reduction reaction), which yields very poor decontamination
- 2) **Chemical reaction** in which the reaction takes place through the electro-generated species (water discharge at the anode to form OH). For example, physically adsorbed "active oxygen" (physisorbed hydroxyl radical (*OH)) or chemisorbed "active oxygen" (oxygen in the lattice of a metal oxide (MO) anode). *OH radical is the second strongest oxidant known after fluorine with high standard electrode potential ($E_0 = 2.80$ V vs. SHE).

With regard to chemisorbed "active oxygen" in the form of metal oxides, organic dyes are selectively transformed into biodegradable compounds usually carboxylic acids and with regard to physisorbed *OH (electrochemical combustion or electrochemi-

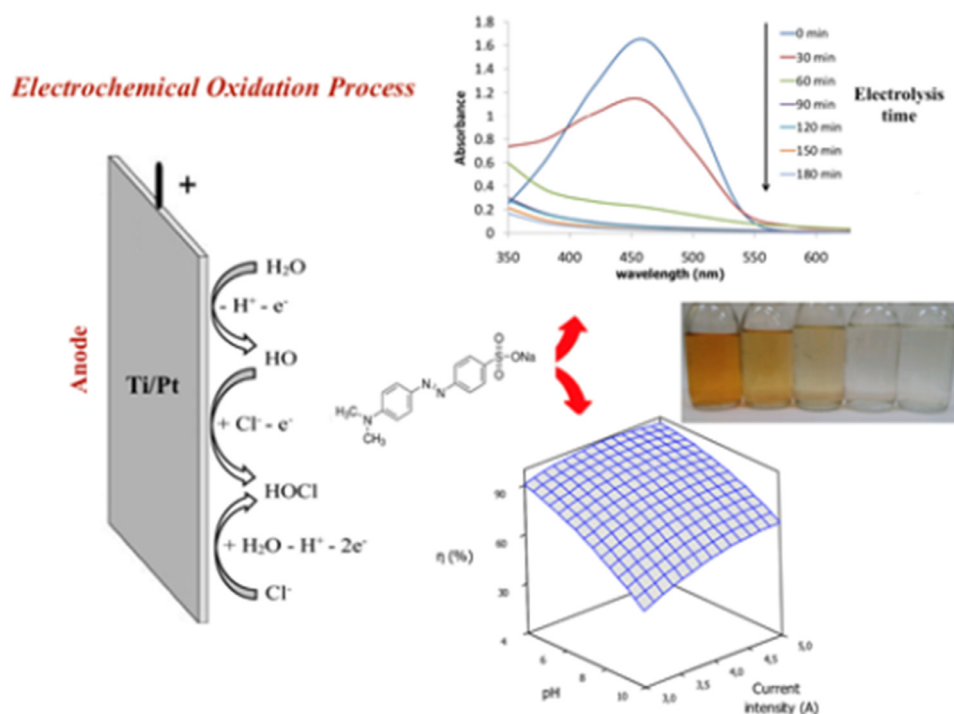


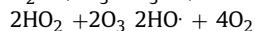
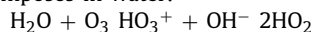
Fig. 1. Schematic representation of electrochemical oxidation process [124].

cal incineration method), organics are completely oxidized to CO_2 and inorganic ions [122].

1) Advanced oxidation processes

The electrochemical oxidation is also known as Electrochemical Advanced Oxidation Processes (EAOP) due to electro-generation of hydroxyl radical as mediated oxidant (Fig. 1). Advanced oxidation could be defined as oxidation by compounds with an oxidation potential (E_0) higher than that of the oxygen (1.23 V), i.e. hydrogen peroxide ($E_0 = 1.78$ V), ozone ($E_0 = 2.07$ V) and the hydroxyl radical ($E_0 = 2.28$ V) [123].

Advanced oxidation processes (AOPs) are therefore mostly based on the generation of highly reactive radical species (especially the hydroxyl radical $\text{HO}\cdot$) that can react with a wide range of compounds. For example: dye molecules. There are four different advanced oxidation processes that have been mostly studied are ozonation, $\text{UV}/\text{H}_2\text{O}_2$, Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and UV/TiO_2 . In the ozonation process, hydroxyl radicals are formed when O_3 decomposes in water:



Although ozone itself is a strong oxidant, the intermediate hydroxyl radicals are even more reactive than the ozone molecules. Further, decomposition of ozone requires high pH (>10) and ozone treatment of organic molecules proceeds therefore faster in alkaline solutions than at neutral or acidic pH where ozone is used as a main oxidant [120,125,126].

1.9.4. Photocatalytic degradation

Conventional methods like biological processes, flocculation, coagulation, filtration, and precipitation are used to remove the dyes from the wastewater, which have drawbacks mainly low removal efficiency [127,128]. Nowadays, several treatment routes were utilized to treat wastewater containing pigment or dye molecules viz., incineration, bio-treatment, ozonation and adsorption processes based on solid adsorbents [119,120,129,130]. However, recent methods also have disadvantages such as (i) production of toxic volatile

constituents in incineration process, (ii) selection of specific enzyme for dye decomposition process is complex, (iii) difficult to get single microorganism to degrade multiple dyes in the textile waste water, (iv) complete degradation of dyes require aerobic process along with anaerobic technique, (v) anaerobic dye degradation gives aromatic amines as by-products which are toxic in nature, and (vi) evolution of foul smell in biological treatment. Further, the parameters such as pH, salt ion content, and temperature of the medium are also affecting the ozonation process [131], which are the main drawbacks for the commercialization for industrial effluent waste or bulk dye removal process. Moreover, the modern dyes were designed to resist both microbial and physico-chemical reactions. Hence, the conventional wastewater treatment techniques including microbial treatment processes are not easy to remove or decompose the most of the dyes. The literature reported earlier also conclude that anaerobic-aerobic techniques may be appropriate, but requires further mineralization process for the decomposition of resulted hazardous aromatic amines. Hence, the detailed studies are needed to go for the decomposition of aromatic amine by-products.

At present photo-catalysis is one of the excellent methods for the degradation of dyes using Reactive Oxygen Species (ROS) generation [2,132]. Photo-catalytic process appears to be a very promising technology in the treatment of endocrine disrupting chemicals (EDCs), however the efficiencies are highly rely on performance of the photo-catalysts [3,133]. Photo-degradation is an important abiotic degradation process in the aquatic environment [10,134]. Many studies have been conducted in the recent years to remove these pollutants using optical catalysts and ascertained that the photo-catalytic degradation process is considered as an eco-friendly method without secondary contamination. In the light-exposure photo-catalysts and electron-hole pairs were created, which are participating in the reaction to accelerate the dye degradation reactions [4,135]. Further, highly safe and the most efficient photo-catalytic processes are used to eliminate the chlorinated phenolic compounds under specific conditions e.g. temperature, pressure and concentration. Mostly, the by-

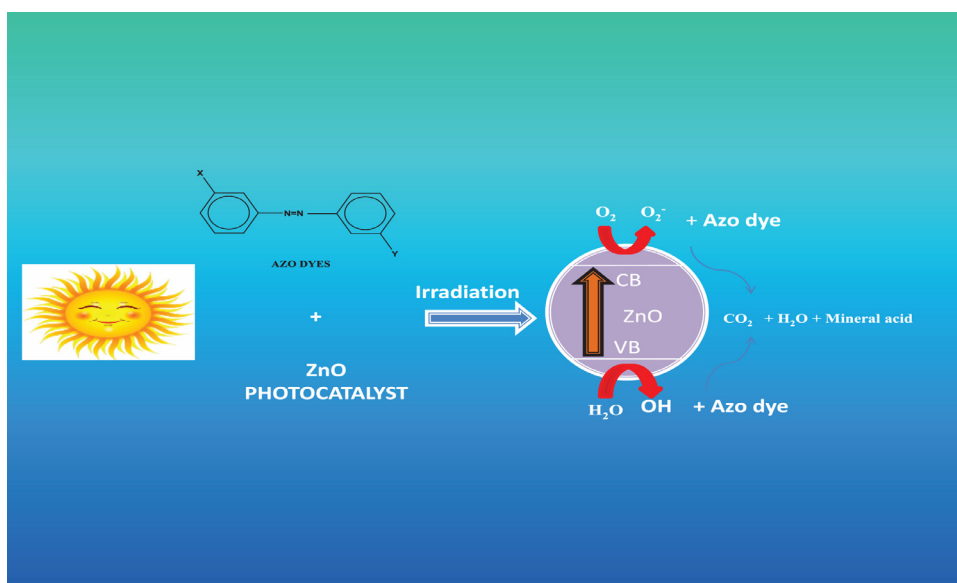


Fig. 2. General representation of photo-catalytic mechanism.

products that resulted from the photo-catalytic process are harmless or having much lower toxicity [5,6,136,137]. In addition to dye degradation, direct photo-degradation in aqueous environments is also considered as one of the most important pathway for pesticide degradation [7–9,138–140]. In short, the process such as photo-chemical mineralization, photo-priming, and microbial photo-inhibition [11,141], altogether are known as photo-degradation [12,142].

So, the heterogeneous photo-catalysis has shown to be a potent technique for solving environmental crisis [143,144]. Heterogeneous photo-catalysis has given way for the development of new semiconductor photo-catalysts to carrying out photo-chemical reactions (Fig. 2). However, the fast recombination rate of the photo-generated electron-hole pairs formed during the photo-degradation process limits the effective degradation.

In order to overcome fast recombination rate of photo-generated electron-hole pairs, the number of research methodologies have been proposed to prepare CuO, ZnO, Fe and TiO_2 nanoparticles coated supported materials for the removal of organic dyes [145–148]. The band gap energy less than 2.5 eV can be effective under solar light or day sun light, but those semiconductor materials with band gap energy greater than 2.5 eV can be used as photo-catalyst under UV light for the dye degradation process [149]. However, the semiconductor photo-catalysts with band gap energy of 2.5 ± 0.3 eV could be effective in both UV and solar lights. Recent researches have focused on the preparation of semiconductors and they are trying to couple the semiconductors with low band gap energy substrates in order to produce UV active catalysts to visible active catalyst with improved surface and catalytic activities. However, different semiconductor materials reported till date to treat the colored wastewater though photo-catalytic methods have several limitations particularly deactivation of most of the photo-catalysts studied. The deactivation caused by ion scavengers in the solution and a low degradation kinetics in the presence of a high content of dyes in aqueous samples were noticed [150].

Titanium dioxide (TiO_2) discovered by Fujishima and Honda [1972] [151], which was proposed to serve as an effective photo-catalyst under ultra- violet irradiation. Titanium dioxide (TiO_2) is a highly stable, nontoxic, cost- competitive [152–154] and it has proven to be an efficient photo-catalyst for the degradation of organic pollutants [155,156]. The literature report stated that

the ZnS nanoparticles exhibit better photo-catalytic activities than that of the TiO_2 nanoparticles [157]. ZnS is a direct wide band gap semiconductor (3.72 eV) and its photo-carrier generation ability has found to be higher than that of the TiO_2 . Hence, ZnS shows enhanced photo-catalytic activities compared to that of the TiO_2 [157]. ZnS has wide variety of applications in the field of LEDs, electro-luminescence, flat panel displays, infrared windows, lasers, bio-devices, optical coating, electro-optic modulator, photo-conductors, optical sensors and phosphors, etc., [158].

In the case of semiconductor nanoparticles, the photo-catalytic reactions are suppressed mainly due to aggregation of nanomaterials, lower adsorption capacity, decreased surface area and recyclability of the catalyst. In order to overcome such drawbacks, the porous materials like silica, alumina, activated carbon [159], fly ash and MCM are used as a supports for metal sulfide or metal oxide photo-catalyst. Therefore, specific surface area and adsorption efficiency of the catalysts were improved. Further, the presence of semiconductors over supporting material inhibits the recombination of electron-hole pair [160,161].

In addition, an inappropriate structure of the interface limits the interfacial charge-transfer process of photo-generated charge carriers and it therefore lowers the photo-catalytic property of nano-composites. To overcome such problems, one type of metal semiconductor could be combined with another semiconductor metal to reduce recombination rate and thereby leading to a remarkable change in the photo-catalytic activity of the resultant catalyst [161]. Therefore, the coupling of two semiconductor materials to get a single composite material is an efficient tool for the spatial separation of electron and hole pairs, which are expected to display an enhanced photo-catalytic performance [162]. This enhanced concept is suitable for the wide range of applications, which are unattainable by single phase system [163–172]. For the occurrence of spontaneous photo-catalytic reaction, the recombination of electron-hole pairs should be greatly reduced, which could improve the charge separation efficiency and the charge carrier life time of the catalysts. Consequently, this will increase the progress of photo-catalytic efficiency of the catalyst, which can be achieved through interfacial charge transfer from catalyst to adsorbed substrate [163–167,173–175]. Hence, semiconductor assisted photo-catalytic reactions have gained remarkable attention towards waste water treatment and environmental remediation applica-

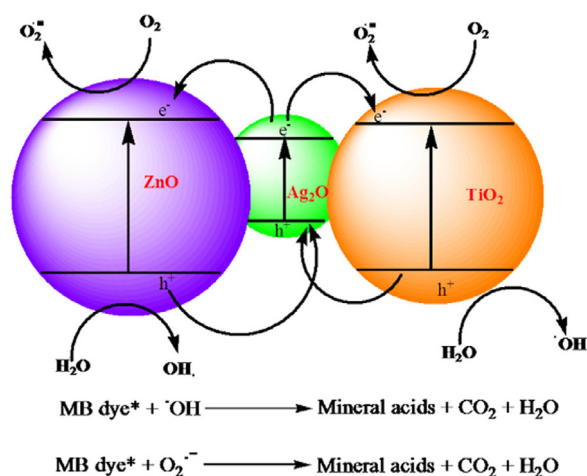


Fig. 3. General dye degradation mechanism of tertiary metal oxide (ZnO/TiO₂/Ag₂O) semiconductor nanocatalyst [161].

tions [176]. General dye degradation mechanism of tertiary metal oxide (ZnO/TiO₂/Ag₂O) semiconductor nano-catalyst is presented in Fig. 3.

To make ZnO semiconductor material as a solar active catalyst, it can be combined with different narrow band gap semiconductor materials like Ag₂O (Fig. 3), which extends its photocatalytic response to the visible-light region [177,178]. According to previous report [179], when ZnS semiconductor was combined with other semiconductors like CdS and Ag₂S, whose band gap energy is lower than that of the ZnS semiconductor, electrons generated from valence band of Ag₂S or CdS are excited to its conduction band and they may be transferred to conduction bands of ZnS semiconductor and holes generated at the valence band of ZnS semiconductor may transferred to conduction band of the Ag₂S semiconductor and vice versa (Fig. 5). This type of probability inhibits the electron-hole recombination effect and thus enhanced photo-catalytic effect was observed when two or more semiconductors were coupled to get a mixed semiconductor catalysts. As per the previous reports, ZnS and CdS semiconductors have the band gap energy value in the range of 3.2 to 3.8 eV [179] and 2.3 to 2.6 eV [180], respectively. Moreover, they have potential applications in the field of light-emitting diodes, optoelectronic devices, photo-catalysis, the phosphors in thin-films, electro-luminescent devices and solar cells [181–183]. The continuous research demonstrated that the development of Ag–CdS [184], PANI–CdS [185], graphene with metal sulphides (MoS₂, Ag₂S, CdS and CuS) [185], SnS₂–MgFe₂O₄/graphene oxide [186], graphene based materials [187], graphitic carbon nitride–metal oxide/metal chalcogenides [188], solar light driven photo-catalysts [189] and graphene–CdS [190] semiconductors for photo-catalysis and hydrogen generation applications. ZnS/CdS nano-catalyst has been obtained through co-precipitation method and its photo-catalytic activity of various dyes has been reported [191]. Further, Ag₂S has received great attention due to its optical and electronic applications such as photo-conductors, IR detectors, super-ionic conductors [192], thermo-electric material and photo-sensitizer for photographic purposes. Ag₂S semiconductor has direct and narrow band gap energy of 1.0 eV [193], which can acts as an effective solar light harvesting semiconductor for photo-catalytic applications [194]. Further, the photo-luminescence studies also confirm that the **tertiary material has lower PL emission peak when compared to that of mono and binary semiconductor systems, which supports the suppression of electron-hole pair recombination and reduction in the defects of the sample surface**. In addition, binary system has lower PL emission peak when compared to that

Table 2
Band gap Energy (E_{bg}) = $1240 / \lambda$.

Photocatalyst	Band gap	C_{BE}	V_{BE}
TiO ₂ (anatase)	3.2	0.3–0.6	2.4–2.7
TiO ₂ (Rutile)	3.0–3.7	–0.05–0.15	2.92–2.95
Fe ₂ O ₃	2.0–2.2	0.3–0.6	2.4–2.7
CdS	2.4	–0.5	1.9
Cu ₂ O	2	–0.7	1.3
WO ₃	2.6–2.8	0.24, 0.4, 0.73	2.99, 3.2, 3.45
SnO ₂	3.8	–0.2	3.9
ZnO	3.2, 3.3	–0.25, –0.2	2.95, 3.1
C ₃ N ₄	2.7	–0.9	1.5
Bi ₂ WO ₆	2.9	–0.1	2.8
SiC	3.26	2.99	–0.27
CdSe	1.7	–0.54	1.16
BiVO ₄	2.4	0.46	2.86
Ta ₃ N ₅	2.1	–0.55, –0.53	1.55, 1.57
TaON	2.4	–0.4, –0.35	2, 2.15
MOS ₂	1.73	–0.04	1.69
GaP	2.25	–0.71	1.54
GaAs	1.4	–0.4	1

of mono semiconductor system. Hence, the ternary catalyst leads to higher photo-catalytic activity than that of the mono and binary catalysts [195].

Similar to metal sulfide semiconductors, the ZnO/TiO₂/Ag₂O metal oxide (Fig. 3) ternary system shows enhanced photocatalytic activity when compared to that of mono and binary metal oxide semiconductor systems [162]. Further, both binary ZnO/Ag₂O and TiO₂/Ag₂O semiconductors possess higher catalytic activity and reduced recombination effect than that of the monometallic semiconductor systems. Hence, to explain the mechanism of the prepared binary or ternary catalyst, the knowledge of energy level of the each semiconductors are essential and some of the energy levels (both valance and conduction bands) are shown in Table 2. Generally, absorption edge from optical absorption (UV-DRS) spectroscopy will give the band-gap energy of the prepared semiconductor materials and the band gap energy can be calculated using the following equation,

In addition, cyclic voltammetry studies also give information of the redox potentials, which is the same as band-gap energy. However, there will be a little difference based on what type of technique used to calculate the band gap energy of the prepared semiconductor catalyst materials, which is due to the difference in the nature of excitation (optical vs electrical band-gap). Further, both these values will slightly differ from the purely theoretical calculated values (i.e. true band-gap). Furthermore, valence band maximum energy can be calculated using X-ray photoelectron spectroscopy (XPS) or UV photoelectron spectroscopy (UPS). The minimum or lower conduction band values can be obtained by adding the band-gap energy to valence band maximum energy obtained from either XPS or UPS studies. In the forth coming sections, the energy level diagrams are drawn and photo-degradation mechanism is explained for another tertiary ZnS/SnS/Ag₂S nano-catalysts. Some of the energy levels of both valence and conduction bands are presented in Table 2 and Fig. 4.

However, the band gap energy values varies with respect to their preparation procedures, size of the particles, nature of the supporting materials, and nature of the metal oxides or sulphides alloying one with another. The band gap energy diagram of some photo-catalysts with respect to the redox potential of different semiconductor materials or chemical species measured at pH of 7 are shown in Fig. 4.

1.9.4.1. Photo-catalytic mechanism of visible active tertiary catalyst .
The photo-catalytic activities of ZnS/SnS/Ag₂S nano-catalysts were mainly due to their enhanced absorption behavior in the visi-

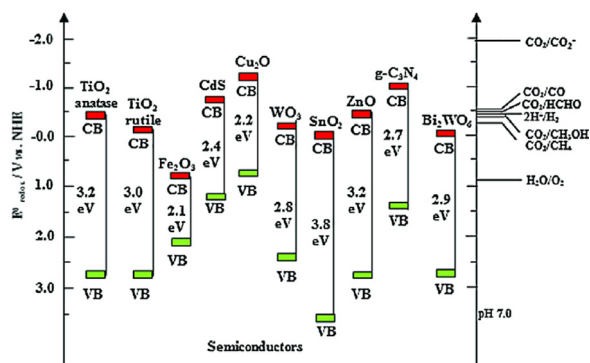


Fig. 4. Band gap energy diagram of some photo-catalysts with respect to the redox potential of different chemical species measured at pH of 7 [194].

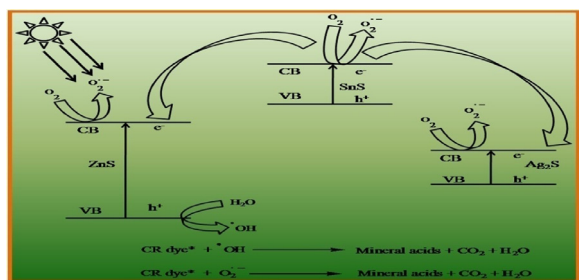
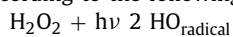


Fig. 5. Schematic illustrations for the mechanism of photo-induced charge carrier transfer in ZnS/SnS/Ag₂S nano-catalyst under solar irradiation [196].

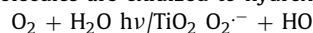
ble region. UV light-active ZnS catalyst was tuned to solar light-active material by coupling with two narrow band gap semiconductor materials such as SnS and Ag₂S semiconductors. Hence, the photo-excitation of electrons becomes easy, which can take place in the presence of solar light illumination (Fig. 5). Meanwhile, the electrons were excited from the valence band (VB) to a conduction band (CB) of the nano-catalyst. As a result, the enriched electrons flow from the VB of SnS to the CB of Ag₂S and ZnS materials and vice versa. The generated electrons (e⁻) react with the dissolved oxygen molecules present in the water to produce superoxide radicals O₂^{•-}. The positively charged hole (h) reacts with the water molecule to form hydroxyl radicals. The report also states that the CR dye molecules degraded by these free radicals will produce simple harmless molecules. The enhancement in the photo-catalytic activity of ZnS/SnS/Ag₂S nano-catalysts was endorsed due to their higher charge separation efficiency of electron hole pairs and inhibition of recombination rates led to an increase in the number of electron hole pairs participating in the photo-degradation process [196].

Generally, photo-catalytic oxidation processes (UV/H₂O₂, UV/TiO₂, UV/Fenton's reagent, UV/O₃ and other) are taking place based on the formation of free radicals under UV or solar light irradiation process. Typically, UV or solar light does not penetrate sufficiently in highly colored waste water, which limits the application of photo-catalytic processes. When UV is used in combination with hydrogen peroxide, hydroxyl radicals are formed according to the following (simplified) reaction:



Drawbacks of UV/H₂O₂ process are relatively high cost and possesses the lack of effectiveness. However, when the photo-catalyst material is irradiated with photons and energy higher than those of band gap energy of the materials, the electrons are promoted from the valence band to the conduction band. The resultant electron-hole pair has a lifetime in the space-charge region that enables its participation in chemical reactions [197]. In

general, oxygen is used to scavenge the conduction band electron to produce super-oxide anion radical (O₂^{•-}), while adsorbed water molecules are oxidized to hydroxyl radicals:



With TiO₂ catalyst under UV treatment, a wide range of dyes can be oxidized. The dyes are generally not only decolorized, but also highly mineralized to CO₂, water molecules and mineral acids [198–214].

Further, the free hydroxyl and super-oxide radicals formation was detected by adding appropriate quenchers like 1,4-benzoquinone (BQ), which is a super-oxide radical (O₂^{•-}) and isopropanol as OH[•] radical scavengers to confirm the generation of oxidative and reductive intermediate species during the solar light illumination (Table 2).

From the results (Table 3), it has been noticed that the addition of isopropanol and 1,4-benzoquinone inhibit the photo-transformation of CR and MB dye molecules. In addition to that, it was observed that the decrease in degradation efficiency occurs with increasing the concentration of isopropanol and 1,4-benzoquinone. The inhibitory effects of isopropanol and 1,4-benzoquinone for the photo-degradation of CR and MB are significant. This is because isopropanol is an OH[•] radical scavenger, which could react with OH[•] radical and quenches the photo-catalytic reactions [215]. Hence, the present investigation concludes that OH[•] radicals were generated during the dye degradation experiments, which could also support the dye degradation mechanism. Further, the inhibition effect of 1,4-benzoquinone authenticates the generation of O₂^{•-} radicals during dye degradation process.[216,217]. The above experimental results conclude that the super-oxide and hydroxyl radicals are the important active intermediate species generated during dye degradation process are responsible for the photo-degradation of CR and MB dye molecules. The analysis of CR and MB dye decomposition has been performed using different analytical techniques. In this regard, the GC and FT-IR studies [218,219] have been performed to support the photo decomposition of the dye molecules by analyzing the product formed during photo-degradation process at different time intervals, which gives complete information about the mechanism of photo-degradation or progress of photo-degradation products. Hence, the development of photo-catalysts are emerging area of research and further extended research in the area is required for commercialization and industrial waste water treatment process.

2. Non-metallic photo-catalytic degradation

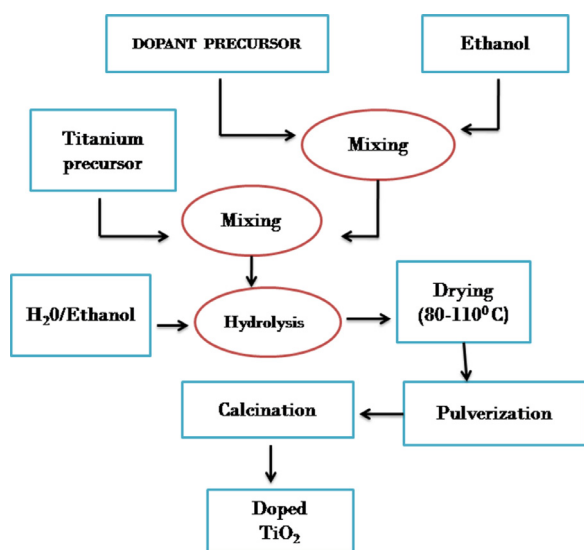
The different strategies have been developed to improve the photo-reduction or photo-oxidation mostly based on metals [220–223]. However, the incorporation of non-metal atoms into the titania structure is still considered as the most popular and effective method, which strengthens the photo-response or photo-degradation process over that of an un-doped materials. Among them, non-metal doped TiO₂ has attracted particular attention because those atoms can be easily introduced into the titania lattice, and changes the electronic structure of the material and finally shifting the optical response towards the visible range.

An extensive research of non-metal doped TiO₂ photo-catalysts are widely carried out since early 1990s [224,225]. Doping with non-metallic anions, and nitrogen in particular has attracted considerable attention in recent years although its effectiveness is still being intensely debated [226–228]. The multi-functional and advanced semiconductor titania (TiO₂) with superior physico-chemical and opto-electronic properties are extensively investigated in wastewater purification, which is mainly due to its non-toxicity, favorable band edge positions, water insolubility, multifaceted electronic properties, surface acid-base properties, and so on. However, large band gap and massive photo-generated charge

Table 3

Shows the effect of isopropanol and 1,4-benzoquinone concentrations (0.1 M and 1.0 M) for the photo-degradation of CR dye and MB dye in the presence of various catalysts [161,162,195,196].

Quencher	CR dye% degradation	CR dye% degradation	MB dye% degradation
	ZnS/SnS/Ag ₂ S (30 min)	ZnS/CdS/Ag ₂ S (30 min)	ZnO ¹ /TiO ₂ ¹ /Ag ₂ O ^{0.25} (30 min)
No quencher	61.70	65.01	40.86
0.1 M Isopropanol	55.25	55.63	36.34
1 M Isopropanol	43.92	42.74	31.91
0.1 M, 1,4benzoquinone	57.42	59.82	–
1 M, 1,4benzoquinone	45.63	47.57	–



Scheme 6. Various steps involved for preparation of non-metals doped TiO₂ using sol-gel method.

carrier recombination hinders its wide application under natural solar light. Hence, altering the surface-bulk structure of titania is a major target in the area of both material and environmental chemistry for its better applications. The substitution of p-block elements (B, C, N, F, S, P, and I) either at Ti⁴⁺ and O²⁻ sites in TiO₂ semiconductor is a promising approach to overcome the fore mentioned drawbacks.

Further, theoretical calculations may be very useful in the design and understanding of the photo-catalytic activity of doped materials. For example, the effects of doping TiO₂ with N, P, B and F, which are the non-metal elements of the p-block in the first row of the Periodic Table have been elegantly modeled by applying the same models, methods and computational setup [226–228]. When lighter elements such as nitrogen, carbon or boron replace oxygen atoms in TiO₂, the introduction of intra band-gap states are responsible for absorption of visible light or modifying the electronic structure of the material, which is ultimately shifting the optical response toward the visible range and thus, the resultant catalyst can be used as visible light or day sun light active photo-catalysts. The following Scheme 6 presents the various experimental steps involved for preparation of non-metals doped TiO₂ through sol-gel methodology (Scheme 6).

Furthermore, a smaller atomic number of the dopant element is associated with greater energy of the corresponding 2p states, because the effective nuclear charge is smaller. The 2p states of B, C and N lay 2.18, 1.39 and 0.13 eV, respectively and the values lie above the top of the TiO₂ valence band. Whereas in the case of the heavier atom like fluorine dopant is completely different, because its 2p states lie below the oxygen 2p valence band. Fluorine element has one electron more than that of oxygen, which is trapped, forming Ti₃⁺ states below the bottom of the TiO₂ con-

duction band [226–228]. Hence, the rate of photo-catalytic activity could be higher when TiO₂ doped with F compared with that of N, C or B.

3. Conclusion

Numerous synthetic dyes are extensively used for textile dyeing and other industrial applications, predominantly contain an azo-chromosphere based groups. Since these dyes are designed to be resistance to microbial and physico-chemical attack, conventional processes of wastewater treatment including biological methods are not possible to destroy most of the synthetic dyes. The available literature provides the information about the physico-chemical and biological methods for the treatment of dye-containing wastewater. The present review article provides an up-to-date survey of various biological and physico-chemical activities of azo compounds including heterogeneous catalytic reactions. It is expected that this review work will be expected stimulates the attention of the researchers who have interest in the development of novel azo-bearing molecules and treatment of azo-dye based industrial effluents.

Declaration of Competing Interest

None.

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